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# Computations of absorption spectra and nonlinear optical properties of molecules based on anthocyanidin structure

**Y. El Kouari · A. Migalska-Zalas · A. K. Arof · B. Sahraoui**

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**Abstract** Simulation of UV–VIS spectra and microscopic third-order nonlinear optical (NLO) coefficients at 532 nm wavelength of molecules based of anthocyanidin structure in gas phase environment using semi-empirical PM3 method was calculated. One-photon absorption characterizations of the investigated molecules have been theoretically obtained by configuration interaction method with doubly occupied molecular orbitals. Estimated theoretical spectra shows a sensibility to the different functional groups such as hydroxyl and methoxyl substitution in radicals. These groups causes red shift in absorption spectra in comparison to the other samples what agree well with the experimental data. Adjunction of such functional donor character group in the investigated molecule slightly decreases the HOMO–LUMO energy splitting gap but increases the ground state dipole moment resulting the substantial increase of NLO coefficient in this system comparing to the other samples. According to presented investigations the tested molecules have large nonlinear optical properties.

**Keywords** Absorption spectra · Red shift · (NLO) coefficient · Anthocyanidin · HOMO · LUMO · Semi-empirical method

Y. El kouari
Département Génie Electrique, Faculté des Sciences et Techniques, Université Hassan II Mohammedia-Casablanca, B.P. 146, 20650 Mohammédia, Morocco

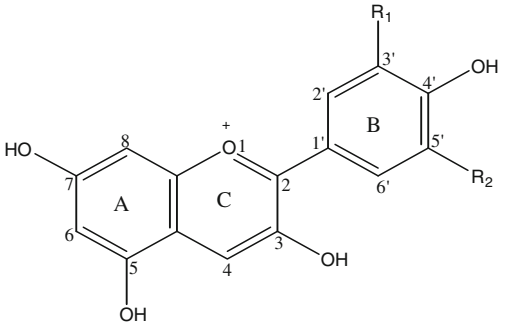
A. Migalska-Zalas (✉)
Institute of Physics, J. Dlugosz Academy of Czestochowa, Aleja Armii Krajowej 13/15, 42217 Czestochowa, Poland
e-mail: aniazal@op.pl

A. K. Arof
Centre for Ionics University of Malaya, Department of Physics, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

B. Sahraoui
LUNAM Université, Université d'Angers, CNRS UMR 6200, Laboratoire MOLTECH-Anjou, 2 bd Lavoisier, 49045 Angers, France

## 1 Introduction

There is a growing interest in expanding the scope of anthocyanins in food and human nutrition, they are considered as potential food colorants used to replace synthetic dye (Andersen and Jordheim 2004; Clifford 2000). Anthocyanins are chemical compounds that absorb light in the visible region. The colour is due to a chromophore that captures light energy and excites an electron from a lower to a higher orbital. Unabsorbed energy is reflected and/or collapse to capture the eye. Nerve impulses are then generated and transmitted to the brain where they are interpreted as a dye (Hari et al. 1994). Considering the stability, natural pigments are less stable in comparison to synthetic dyes, but their development and the use has attracted much attention (Delgado-Vargas and Paredes-López 2002). Natural pigments substituted synthetic dyes are widely used in the food and pharmaceutical industries due to the no negative effects on health. Anthocyanin is a flavonoid chemical group. This is one of the main groups of natural pigment safter chlorophyll, which is visible to the human eye. In flowers, anthocyanins can be found mainly in the cells of the epidermis, and only occasionally in mesophylls. Anthocyanins absorb light in the red range and are responsible for the blue, purple, violet, purple, red, orange, and the color of plants (Jackman and Smith 1996). The colors range depends on the degree of oxygenation and anthocyanidin and nature of substituents, for example, the sugar moiety added to the chromophores (Schwinn and Davies 2004). Anthocyanidin is central chromophore of anthocyanin. The basic structure of anthocyanins is shown in Fig. 1.




| *Sample* | Substitution pattern | | $\lambda_{max}$ *[nm]* Visible spectra exp |
|---|---|---|---|
| | $R_1$ | $R_2$ | |
| Pelargonidin | H | H | *494* |
| Cyanidin | OH | H | *506* |
| Delphinidin | OH | OH | *508* |
| Peonidin | $OCH_3$ | H | *506* |
| Petunidin | $OCH_3$ | OH | *508* |
| Malvidin | $OCH_3$ | $OCH_3$ | *510* |

**Fig. 1** Chemical structures of studied molecules (Wrolstad et al. 2005)

Anthocyanins are materials interesting for study the linear, nonlinear optical properties and electronic transfer processes in view of electron donating and electron accepting character. Nonlinear properties of the particles depend on how electrically charged particles—usually positive ions or electrons—can interact with light and move from the position of equilibrium, and on the charge dencity distribution within the material. The combination of donor and acceptor groups through π conjugated bonds is a good strategy to obtain particles with a high value of non-linear optical hyperpolarizability.

This work is devoted to theoretical calculations of UV spectra and second-order frequency-dependent molecular hyperpolarizability to propose NLO analysis of these complexes on a molecular scale.

For the numerical analysis, the electronic states obtained in the semi-empirical PM3 approximation within a framework of the Restricted Hartree-Fock approach with the singly excited configuration interaction method are used. Semi-empirical methods offer a quick and cheap way to predict the nonlinear-optical properties. Semi-empirical PM3 method is powerful tool for excited states properties such as oscillator strengths and excitation energies of large molecular. Moreover is very apropriate method to calculate linear and nonlinear optical properties of large molecules. Second-order hyperpolarizability (γ) of the molecules have been calculated using the sum-over-state (SOS) method for the degenerate four wave mixing (DFWM) process at several incident frequencies. The quantum chemical calculations give important information relating to the changes of propriety of material using the suitable substituent group. Especial attention will be devoted to the delocalisation of π electrons along the molecular backbone influence of different functional group on the output of third order optical properties and a spectral shift of UV absorption.

## 2 Theoretical simulation

Before performing quantum-chemical calculations were performed to optimize the geometry of investigated molecules. Since the optimized structure of the molecule depends on the values calculated in the following steps based on the geometry of the molecule, so the exact optimization performed to find the global minimum.The initial geometries of the anthocyanins have been calculated at restricted Hartree–Fock (HF) level with the standard 6-31G basis set in C1 symmetry using ab initio methodology implemented in Gaussian (Frisch et al. 2004) programme packages. The linear and nonlinear optical properties of the investigated molecules were calculated using methodology implemented in HyperChem 7.5 program packages.[1] All quantum chemical calculations were performed by semi-empirical PM3 (Dewar et al. 1985; Dewar and Dieter 1986) method within a framework of the restricted Hartree-Fock approach and convergence limit up to $10^{-6}$ eV after 500 iterations was achieved. The calculations mixes all single determinant wavefunctions that can be obtained from the ground state by exciting electrons from a subset of the occupied orbitals to a subset of the unoccupied orbitals. The subsets are specified as an energy criterion associated with the energy difference between the occupied orbital and the unoccupied orbital. The electronic spectra were calculated by the configuration interaction (CI) method with the maximum excitation energy up to 10 eV. Local perturbation were considered only within a framework of the isolated molecule in vacuum. The influence of the intermolecular electron vibration interactions is not taken into account. The intensity of absorption was expressed by the following formula:

[1] HyperChem Professional 7.51, Hypercube, Inc., 1115 NW 4th Street, Gainesville, Florida 32601, USA.

$$\varepsilon_{x,y,z} = \omega \sum_{j=1}^{N} \left|\mu_j^{(x,y,z)}\right|^2 \exp\left(-\left(\frac{E - E_j}{H}\right)^2\right) \tag{1}$$

where j—number of transition from ground state, $E_j = \hbar\omega_j$—transition energy, $\mu_j^{(x,y,z)}$—transition dipole component (Migalska-Zalas et al. 2008). The empirical parameter H was chosen at reasonable value of 0.5 eV, what gives the best agreement in line shipe of calculated spectra comparing to experimental results.

The PM3 semi-empirical method is used for the interpretation of ultraviolet spectral data since this technique is suitable to the calculation of exited state properties such as oscillator strengths and excitation energies. In this case it is possible to determine the hyperpolarizability via the sum-over-states formulation.

The total dipole moment induced by the electric field $\mu_{ind}$ is often write as a Taylor series expression in the electric field F. Here $\mu_0$ is the permanent dipole moment, $\alpha$ is the linear polarizalility, $\beta$ and $\gamma$ are the suitable hyperpolarizability.

$$\mu_{ind} = \mu_0 + \alpha^T F + \frac{1}{2!}\beta^T F^2 + \frac{1}{3!}\overset{T}{\gamma} F^3 + \ldots \text{where,} \quad F = F_o + F_\omega \cos\omega t \tag{2}$$

In this case the energy expression is a simply related to equation (2). The sum-over-states expression for $\gamma$ comes from the fourth order term in expansion (3).

$$E = E_0 - \alpha^T F - \frac{1}{2!}\alpha^T F^2 - \frac{1}{3!}\beta^T F^3 - \frac{1}{4!}\overset{T}{\gamma} F^4 \ldots \tag{3}$$

When the interacting beam are at the same frequency (how it is in the case of DFWM experiment Sahraoui and Rivoire 1997) the expression described the values of second order hyperpolarizabillity simplified to the Eq. (4) and may be described in terms of the different energy levels from g to n,of the molecule.

The values of second order hyperpolarizabillity may be expressed in terms of different energy levels from g to n,of the molecule.

$$\underset{ijkl}{\gamma} = K \sum_{g=1}^{n} \frac{\left|\mu_i^{(g)}\right| \left|\mu_j^{g}\right| \left|M_k^{(g)} - M_k^{(0)}\right| \left|M_l^{(g)} - M_l^{(0)}\right|}{(E_g^2 - (2\hbar\omega)^2 + H)} \tag{4}$$

where $\mu_i^{(g)}$, $\mu_j^{(g)}$ are the transition dipole moment between the high occupied molecular orbital (HOMO) and the exited state, $\left|M_k^{(g)} - M_k^{(0)}\right|$—difference between the excited (configuration interaction (CI) level) state dipole moment and ground state one, $E_g$- transition energy from the ground to exited state, $\hbar\omega$ is the energy of a incident laser photon, H determines the line shape broadening, n is a number of exited state. Indices i,j,k,l = x,y,z are defined as laboratory Coordinate Cartesian system. In a present work we calculated $\gamma_{xxxx}$, where the x-direction corresponds to the maximal permanent dipole moment (Oudar and Chemla 1977). The calculated values of the nonlinear optical hyperpolarizabilities are presented in the Table 2.

## 3 Results and discussion

The calculated spectrum for the investigated molecules are presented in Fig. 2. These spectra present the typical absorption band at 200–600 nm from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). From the calculated

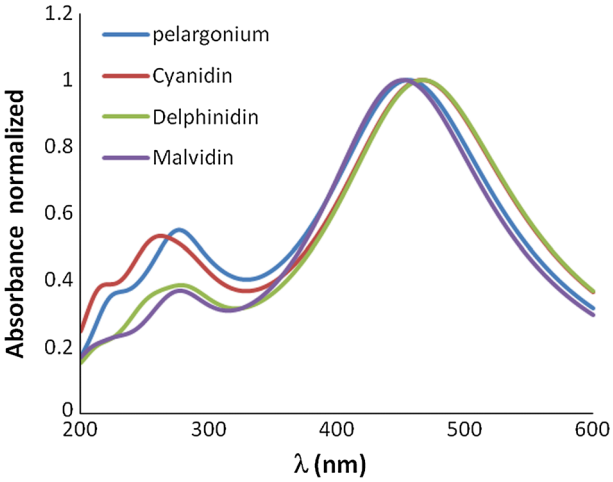



**Fig. 2** Calculated absorption spectra within the PM3 semi empirical model for the investigated compounds

spectrum some characteristic bands responsible for charge transfer can be observed. The bands in the range of 300–500 nm were assigned to $\pi - \pi^*$ transitions and localized over the whole complex. There are also the bands in the region between 200 and 300 nm involving mainly $\pi \rightarrow \pi^*$ transitions due to C=O and C=C groups. The position of the first UV–VIS absorption peaks position of the calculated spectra using semi empirical model and experimental one are presented in the Table 1. As shown in Fig. 2, the $\pi - \pi^*$ band of the: Delphinidin, Petunidin, Malvidin, hydroxyl OH and methoxy OCH3 containing-group systems are shifted to the red compared to the others molecules. The fact that this system exhibits maximum absorption at the longest wavelength among the investigated compound reflects the highest charge-transfer interaction occurring between the electron-donor-acceptor group in the gas phase. The calculated transition energies are generally in good agreement with the experimental results (Table 1), differences being typically $< 40$ nm for all investigated compounds. The position of the $\lambda_{max}$ of the measured spectra is shifted to the region of larger wavelengths with respect to the calculated spectra. The reason of this disagreement between the theoretical and experimental results of absorption spectra could be a quantum chemical calculations without taking into account interaction between molecule and solvent polarity (Reichardt 1988) because the absorption spectra of organic molecules in liquid solutions are known to be depend on the local electric fields generated by the surrounding polar molecules of solvent. One can conclude these molecules the vibration and inter-molecular chromospheres—solvent contributions can be very important.

The calculated HOMO and LUMO gaps as well as total dipole moments are presented in the Table 1. The latter play important role in the NLO properties. One can see that for the moleculs Delphinidin, Petunidin, Malvidin HOMO-LUMO energy splitting gap is slightly decreased than for the remaining samples. A very important parameter is a difference between the ground and exited dipole moments. We can see that the methoxy and hydroxyl groups presented in these molecules decrease HOMO–LUMO energy splitting gap but icrease the ground state dipole moment comparing to the other samples what enlarges NLO coefficients. A large dipole moment leads to a increasing of second-order hyperpolarizabilities in these systems what it results directly from Eq. 4.

**Table 1** Values of calculated linear optical properties. Total dipole moments, HOMO, LUMO, HOMO–LUMO optical gap, first UV–VIS absorption peak position (theory and experiment)

| Sample | $\lambda_{max}$ (nm) Exp. | $\lambda_{max}$ (nm) Theor. | $\mu$ (D) | HOMO | LUMO | $\Delta E_{HOMO-LUMO}$ (eV) |
|---|---|---|---|---|---|---|
| Pelargonidin | 494 | 465 | 2.65 | −12.13 | −5.87 | 6.26 |
| Cyanidin | 506 | 475 | 4.07 | −11.98 | −5.92 | 6.06 |
| Delphinidin | 508 | 476 | 5.63 | −11.91 | −5.95 | 5.96 |
| Peonidin | 506 | 476 | 4.22 | −11.92 | −5.87 | 6.05 |
| Petunidin | 508 | 472 | 6.29 | −11.84 | −5.85 | 5.99 |
| Malvidin | 510 | 468 | 6.84 | −11.81 | −5.87 | 5.94 |

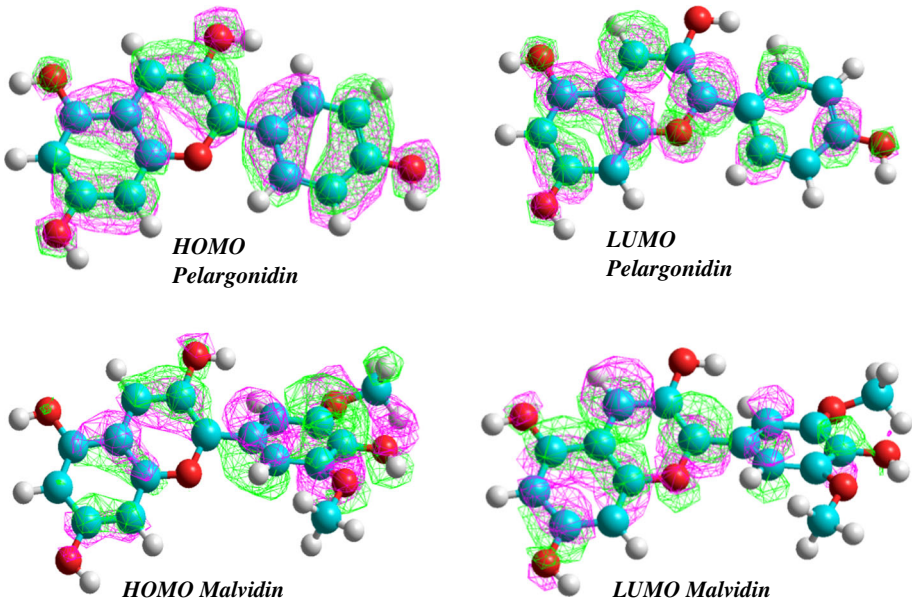



**Fig. 3** Electrostatic potential distribution HOMO and LUMO for Malvidin and Pelargonidin

One the other hand, we have also calculated one electron energy eigenvalues and LUMO contours showed in Fig. 3. Overlap between the HOMO and the LUMO is a governing factor in many reactions. An example of Frontier Orbital theory is in predicting sites of electrophilic attack aiming to join of electrons on aromatic compounds. If we plot the HOMO as a contour map, the region of highest density is generally the site of electrophilic attack. This is generally the site of reaction. In this example, the HOMO is plotted one Å above the plane of the molecule. It shows the place of electrophilic attack at the naphthalene group.

Particularly we show that the non-centrosymmetry of the charge density could lead to a substantial enhancement of the total dipole moments as well of the corresponding transition dipole moments between the HOMO states and excited CI states.

We should point out the fragments contributing to the obtained results and we present only the largest contributions connected with influence the MO wave functions. In this case main role belongs to the fragments containing the donor methoxy and hydroxyl groups.

**Table 2** Values of calculated nonlinear optical properties

| Molecule | $\gamma_{XXXX}$(ESU) CALCULATED AT $\gamma$ 532nm $\times 10^{-36}$ | $\lambda_{XXXX}$(ESU) CAL. Maximal and $\gamma$ (NM) For which was obtained $10^{-32}$ | |
|---|---|---|---|
| Pelargonidin | 8.05 | 38.50 | 439 |
| Cyanidin | 39.70 | 4.32 | 431 |
| Delphinidin | 40.40 | 2.52 | 488 |
| Peonidin | 28.20 | 5.15 | 482 |
| Petunidin | 34.80 | 240.00 | 519 |
| Malvidin | 113.00 | 41.60 | 386 |
| $CS_2$ | 39.5 | – | – |

The presented contours also show how the small change of the backside group, chemical bonds may change the total molecular charge density distributions. The attached various radicals in the molecules play a central role in determining the electron charge density non-centrosymmetry what determines the third-order nonlinear optical properties described by fourth rank polar tensor. A higher charge delocalization is observed for Malvidin possessing two methoxyl groups as radicals. Let's compare for example the large difference in charge density distribution in the HOMO and LUMO for this compound with the excellent molecular hyperpolarizability $\gamma$ obtained for the mentioned molecule. The highest density in the HOMO state is situated over the donor groups then charge jump over from one part of molecule to the other, what causes a large asymmetries of molecule, and the large change of dipolar moment in basic and excited state. At the same time absence of hydroxyl and methoxy groups compensates the gradients of the charge density resulting in essential decrease of the nonlinear optical coefficient (see Table 2). Such investigations give a possibility to operate by the chemical bonds in desirable direction in order to achieve an enhanced of the optical susceptibilities of higher orders. These maps give imagine about possible ways to perform molecular engineering manipulation within the presented compounds.

We present the calculated third-order nonlinear optical coefficients for the investigated molecules in the Table 2. The theoretical calculations show that the second-order hyperpolarizabilities $\gamma$ strongly depends from the wavelength of incident electromagnetic radiation. The obtained values of second order hyperpolarizabilities are highest than the nonlinear coefficients obtained for similar molecules in Ref. Sahraoui and Rivoire (1997). From calculations it results that Malvidin is the best candidate from among studied molecules for nonlinear optical investigation using laser wavelength close to 532 nm. We can see substantial increase of the cubic hyperpolarisability close to 532 nm $\gamma_{xxxx} = 1.13 \times 10^{-34}[esu]$ in the Malvidin. From the Table 2 it can be noticed that the absolute values of third order nonlinear optical coefficient of Malvidin is about two order bigger than for pelargonidin and one order bigger than for other molecules. It can be explained by presence of two methoxyl group in molecule favouring electron delocalisation and in addition this molecule is more stabilised owing to pronounced large dipole moment presented in the Table 1.

The calculated second hyperpolarizabilities for the investigated molecules have the values comparable to the similar compounds reported in Refs. Migalska-Zalas et al. (2012), Bouchouit et al. (2010), Karakas et al. (2012). Anthocyanins are radicals of different natures, one donor and one acceptor and have a large third-order nonlinearity since the radicals add their effects, thus intensify the asymmetric distortion of the conjugated system. Further the electronic properties of this type of molecule exhibit a unusual property, the intramolecular (Kelly et al. 2005) charge transfer between the two radicals.

## 4 Conclusions

We have investigated contribution of the different functional groups in Anthocyanins to the output of nonlinear coefficient as well as a UV spectra. Good agreement between the theoretically calculated and experimentally measured spectra was observed. Analysis of the theoretical spectra shows a substantial sensitivity to the backside groups. The theoretical calculations show that the second-order hyperpolarizabilities $\gamma$ strongly depends from the wavelength of incident electromagnetic radiation. Different moieties causes the substantial changes of non-linear optical coefficients. As shown in Fig. 2, the $\pi - \pi^*$ bands of the Delphinidin, Petunidin, Malvidin containing hydroxyl and methoxy groups are shifted to the red compared to the: Pelargonidin, Cyanidin and Peonidin. One found that the hydroxyl OH and methoxy OCH3 containing-group exhibits maximum absorption at the longest wavelength among the investigated compound reflects the highest charge-transfer interaction occurring between the electron-donor-acceptor group in the gas phase. That fact stimulates increasing of NLO coefficient. The results of quantum chemical calculations can provide the basis for finding of compliance of the calculated and experimental electronic properties in such kinds molecules.

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